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Edge effects in the two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnet

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We use quantum Monte Carlo simulations to study effects of free edges in the two-dimensional spin-$\frac{1}{2}$ Heisenberg antiferromagnet. We find that the magnetic response of an edge is smaller than the bulk susceptibility. This counterintuitive quantum effect can be traced to enhanced antiferromagnetic nearest-neighbor spin correlations, i.e., tendency to local singlet formation, at and close to the edge. These correlations form a comblike pattern, which can be reproduced with a simple variational valence-bond state. We also study rough edges and find that these instead significantly enhance the susceptibility due to local sublattice imbalance impeding singlet formation.

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Among the many complex properties of correlated quantum systems, the roles of defects, such as impurities and boundaries, are intriguing. Defects inevitably effect experiments to an extent often not precisely known. On the other hand, they can also serve as useful experimental probes of correlated quantum states.[1–4] Theoretically, impurity effects in quantum antiferromagnets have been studied extensively in one[5,6] and two dimensions.[7–12] Impurities can effectively cut isolated spin chains into finite segments with free ends, which leads to particularly strong deviations from bulk magnetic properties in one dimension.[5] A good example is the quasi-one-dimensional antiferromagnet Sr_2CuO_3, for which the NMR line exhibits a broad background,[2] which is well accounted for by the local magnetic-susceptibility (Knight-shift) distribution of open-end Heisenberg chains.[2,5] In two dimensions, free edges can be expected to have less dramatic consequences because of the typically small ratio of boundary to bulk, and not much attention has been paid to them. However, with the increasing focus on nanoscale materials, the boundary physics should become accessible (or unavoidable depending on the perspective) also in two-dimensional antiferromagnets. It is therefore important to establish what edge effects to expect based on prototypical model systems such as the Heisenberg Hamiltonian. In this Rapid Communication we take some steps in this direction.

We use the approximation-free stochastic series expansion (SSE) quantum Monte Carlo method[13] to study the antiferromagnetic ($J>0$) Heisenberg Hamiltonian,

$$H = J\sum_{\langle i,j\rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where $\mathbf{S}_i$ are the usual $S=\frac{1}{2}$ spin operators and $\langle i,j\rangle$ denotes nearest neighbors on a square $L\times L$ lattice. We consider systems with completely open boundaries as well as semiopen ones, which are periodic in one direction and open in the other direction. The absence of corners and the translational symmetry along the open edges in the semiopen systems allow easier access to an infinite edge. On the other hand, it is also interesting to study corner effects in the fully open systems. Experimentally, it is likely that typical samples would have some roughness, leading to effects not captured by the smooth edges of the $L\times L$ lattices. We therefore also study systems with irregular edges constructed according to a scheme described further below. We are interested in the magnetic response of the edges and will also investigate how this is related to changes in the spin-spin correlations relative to those in fully periodic systems.

In analogy with the impurity susceptibility previously considered for systems with isolated vacancies or added spins,[9,10] we define an *edge susceptibility*,

$$\chi_E = (\chi_a - \chi_0)/aL, \tag{2}$$

where χ_a is the total magnetic susceptibility for a system with a free edges; $a=0$ for periodic systems, $a=2$ for semiopen boundaries, and $a=4$ for fully open systems. In all cases there are $N=L^2$ spins and the total susceptibilities are given by

$$\chi_a = \frac{1}{T}\langle M_z^2\rangle, \quad M_z = \sum_{i=1}^{N} S_i^z. \tag{3}$$

The normalization with aL in Eq. (2) reflects the natural assumption that the difference in response should scale with the total length of the edges of the open or semiopen systems. One would intuitively anticipate $\chi_E>0$, as the edge spins should be free to fluctuate more than those in the bulk. Surprisingly, this actually does not hold when $T\ll J$ and $L\to\infty$. Figure 1 shows the temperature dependence of χ_E for semiopen systems. The scaling of $\chi_2-\chi_0$ with the edge length is confirmed as the χ_E curves for different L coincide for increasing L. For $T\gg J$, the spins contribute independently $(4T)^{-1}$ to the susceptibilities and, consequently, χ_E vanishes. In the limit $T/J\to 0$, we must have $\chi_E\to 0$ for any (even) L because the ground state is a singlet regardless of the boundary condition (i.e., $M_z=0$), which is seen explicitly for $L=4$ and 8. Focusing on the $L\to\infty$ converged data, decreasing T initially leads to an increasing χ_E, in line with the expectation of $\chi_2>\chi_0$ due to enhanced fluctuations of the edge. However, a maximum is reached at $T/J\approx 0.5$, below which χ_E decreases and becomes negative. The temperature dependence below $T/J\approx 0.1$ is consistent with a logarithmic divergence; $\chi_E\propto -\ln(J/T)$. This behavior can be contrasted with the single-impurity susceptibility, which, for both va-

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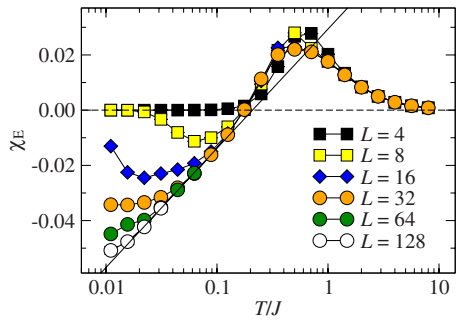

FIG. 1. (Color online) Edge susceptibility of semiopen systems. Error bars are smaller than the symbols. The line is a logarithmic-linear fit to the size-converged data.

cancies and added spins, is always positive when $T\to 0$, diverging as a Curie form with a logarithmic correction.[9,10] In the case of the edge problem considered here, where the defect is nonmagnetic (the number of spins is the same in the periodic and open systems), there is no *a priori* reason to expect a divergent χ_E. We have also run simulations for the classical Heisenberg antiferromagnet with semiopen boundaries and in that case find χ_E to converge to a positive constant as $T\to 0$. Thus, the negative divergent edge susceptibility is a purely quantum-mechanical effect.

When normalized by the total number of spins L^2, instead of the edge length L, the divergent edge susceptibility would be a negligible correction to the bulk susceptibility, which is constant as $T\to 0$.[14] However, in principle a local susceptibility can be accessed in NMR experiments through the Knight shift,[2,15] and provided that sufficient sensitivity can be achieved and the edges are smooth enough (both of which may clearly pose challenges), the divergence should be detectable. We thus also study the spatially resolved susceptibility defined for a site i as $\chi_a(i)=\langle S_i^z M_z\rangle/T$. For a periodic system, $a=0$, there is no dependence on the location i, whereas in the semiopen system $\chi_2(i)$ depends only on the distance R of i from the edge; in either case $\Sigma_i\chi_a(i)=\chi_a$. We define the position-dependent edge susceptibility,

$$\chi_E(R)=\chi_2(R)-\chi_0/L^2, \tag{4}$$

which obeys $\Sigma_R\chi_E(R)=\chi_E$. Figure 2 shows this quantity at

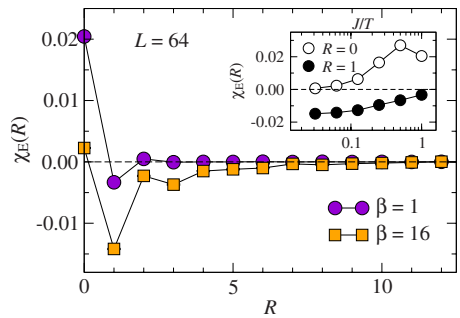

FIG. 2. (Color online) Position-dependent edge susceptibility at distance R from the free edge of a 64×64 semiopen lattice at two different temperatures. The temperature convergence for $R=0,1$ is shown in the inset.

two different temperatures at which the results are size converged for $L=64$. Here it is seen that a large contribution to the negative edge susceptibility comes from the second line of spins from the edge, $R=1$. The response of the edge line, $R=0$, is always larger than the bulk value, however, and $\chi_E(0)$ seems to vanish or become very small as $T\to 0$. Beyond $R\approx 10$, $\chi_E(R)$ becomes very small, indistinguishable from zero, also for the lower temperature. The available data suggest that $\chi_E(R)$ should become negative for any R at sufficiently low T (and $L\to\infty$). Considering the logarithmic divergent χ_E, we should have $\chi_E(R)\propto R^{-1}$ when $T\to 0$.

We will next show that the negative edge susceptibility is related to enhanced local spin correlations close to the edge. The spin correlators $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ for nearest-neighbor sites i,j (bonds) form a pattern of weak and strong bonds.[16] These correlations provide a measure of the amplitude of spins i,j forming a singlet. In addition to calculating the correlations with the SSE method, we have also used a variational state in the valence-bond basis, from which some additional insights are gained.

A valance-bond basis state for N spins is a product of $N/2$ singlets $(a,b)=(\uparrow_a\downarrow_b-\downarrow_a\uparrow_b)/\sqrt{2}$, where a and b are sites on different sublattices of the bipartite square lattice. Any singlet state $|\Psi\rangle$ can be expanded in this overcomplete basis,

$$|\Psi\rangle=\sum_v \psi(v)|(a_1^v,b_1^v)\cdots(a_{N/2}^v,b_{N/2}^v)\rangle, \tag{5}$$

where $v\in\{1,\ldots\frac{N}{2}!\}$ labels the different bond configurations. In the amplitude-product state of Liang *et al.*,[17] the wave-function coefficients are products of real amplitudes $h(a,b)$,

$$\psi(v)=\prod_{i=1}^{N/2} h(a_i^v,b_i^v). \tag{6}$$

For a periodic system the amplitudes depend only on the bond lengths (the x and y separations of the two sites), $h(a_i^v,b_i^v)=h(x_i^v,y_i^v)$, but in an open system they depend on both site coordinates (up to reflection and rotation symmetries). It is known that the periodic Heisenberg model can be very well described by this simple state.[17,18] The amplitudes decay as $h(r)\sim r^{-3}$, where r is the bond length.[18] To study boundary (including corner) effects, we have optimized all amplitudes for a 16×16 fully open lattice using the optimization method discussed in Ref. 18. Also in this case the amplitude-product state provides a very good description of the system, with the energy deviating by less than 0.1% from the approximation-free result obtained using the SSE method at very low T. The bond pattern is also almost identical in the variational and SSE calculations; the result is shown in Fig. 3(a). The correlations are strongest at the corners, and at the edge they form a comblike pattern. This comb structure is repeated on alternating columns away from the boundary, with a rapidly decaying amplitude, as shown in Fig. 4 based on SSE calculations (where only the comb closest to the edge is clearly visible). The strongest bonds are enhanced by more than 10% compared to the bulk. This enhancement is associated with higher amplitudes for local singlets within the combs, which is clearly consistent with the reduced edge susceptibility. The correlation modulations are seen in Fig. 4

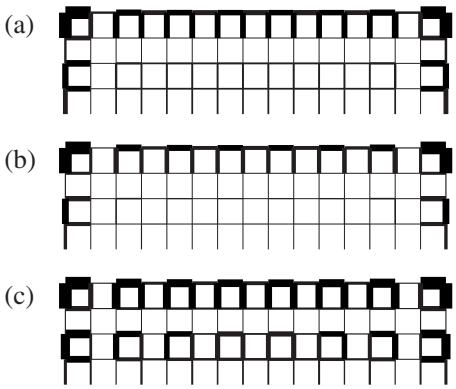

FIG. 3. Bond patterns at an edge of an $L=16$ system obtained with (a) an optimized amplitude-product state (almost exact), (b) a state with amplitudes $h(r)=e^{-r}$, and (c) classical dimers. The linewidths correspond to $-\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ in the range [0.315,0.451] and [0.316,0.466] in (a) and (b), respectively, and average dimer occupation $\in [0.167, 0.500]$ in (c).

to decay more rapidly with R than the edge susceptibility in Fig. 2. On the other hand, the nearest-neighbor correlations represent only the dominant contribution to local singlet formation, and thus the two properties are not easily related to each other quantitatively.

In order to elucidate the origin of the comblike bond pattern, as well as the plaquette structure at the corners, we have calculated the correlations also in a nonoptimal state where the bond amplitudes are very short ranged, $h(r)=e^{-r}$, which corresponds to a spin liquid.[17] In spite of this state being very different from the actual Néel ground state of the Heisenberg model, a very similar bond pattern forms at the corners and edges of the open lattice, as shown in Fig. 3(b). This indicates that the edge pattern is rather insensitive to the long-range correlations of the state—it is essentially governed by the hard-core nature of short valence bonds. To further illustrate this point, we show in Fig. 3(c) the bond-occupation pattern of the classical dimer model (with only short bonds averaging over bond configurations using Monte Carlo sampling). Here there is more of a tendency to plaquette formation at the edge, which, however, changes into a uniform

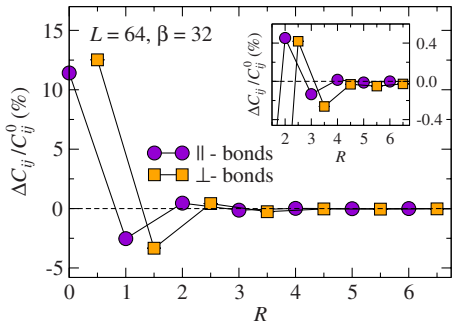

FIG. 4. (Color online) Deviation $\Delta C_{ij}=C_{ij}-C^0_{ij}$ of the nearest-neighbor correlation $C_{ij}=|\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle|$ from the bulk value C^0_{ij} versus the distance R from an edge of an $L=64$ semiopen system at $T=J/32$. Integer and half-integer R correspond to bonds ij parallel and perpendicular to the edge, respectively. The inset shows magnified $R \geq 2$ data.

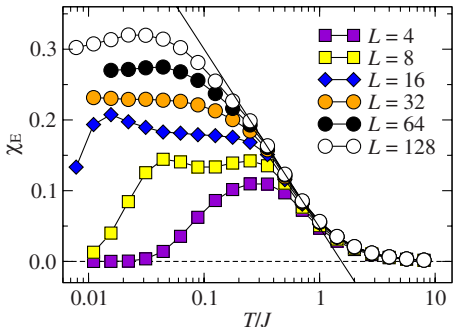

FIG. 5. (Color online) Edge susceptibility for systems with rough edges. The line is a fit to the size-converged intermediate-T data.

comb structure away from the corners of larger lattices. These results show that the gross features of the boundary correlation pattern of the Heisenberg model is dominated by the quantum entropy of short valence bonds, and thus we argue that this is at the heart also of the reduced edge susceptibility.

The site-dependent susceptibility $\chi_a(i)$ can be used to derive experimental consequences, such as the NMR line shape.[2,11] However, it is unclear whether the edge effects we have discussed so far could be observed experimentally. Samples consisting of extremely small fragments are most likely required to distinguish any edge features from the NMR bulk signal, and the fragments appearing in powders hardly have long smooth edges; more likely they have irregular shapes. In principle one could carry out simulations for a suitable ensemble of clusters. Not knowing the actual structure of clusters that could be expected in experiments, we here consider a simple model for roughness added to the $L \times L$ open systems discussed above, with the aim of studying the robustness of the smooth-edge effects.

Our roughness model amounts to traversing all the $4(L-1)$ boundary sites of an $L \times L$ lattice, removing a spin with probability p or coupling a new spin to it with probability p (and doing nothing with probability $1-2p$). In order to have the same number of spins in the periodic $L \times L$ systems and these rough-boundary systems, we only study samples with the same number of added and removed spins, and, furthermore, we only consider clusters with equal numbers of spins on both sublattices (so that the total ground-state spin remains 0). The impurity susceptibility χ_E [Eq. (2)] then still vanishes for finite L both in the limits $T \to 0$ and $T \to \infty$. Figure 5 shows results averaged over several hundred random boundaries for each L. Here $p=1/3$, corresponding to maximum roughness. We again observe a nontrivial logarithmic divergence, but, in contrast with the smooth edge, χ_E is always positive. The prefactor is about five times larger than in the smooth-edge case. Thus we conclude that the roughness has completely changed the nature of the edge effect. For less rough boundaries (smaller p) the prefactor of the logarithmic divergence is reduced, and for some very small p we expect to recover the negative factor pertaining for the smooth boundaries. We have not yet carried out systematic studies of this, however.

Within the picture of the reduced susceptibility of the

smooth edge arising from local singlets, the different responses of the rough edges can be understood as an impeded singlet (short valence bond) formation due to local sublattice imbalance. This has been previously examined in diluted systems (randomly placed vacancies).[19] In that case, as the percolation point is approached local sublattice imbalance leads to localized magnetic moments, which interact and form low-lying states at an energy scale below the normally lowest-lying "quantum rotor" states of the Heisenberg antiferromagnet on finite clusters. Here, for the rough-edge problem, we have only studied the static magnetic response, but it would clearly be interesting to study also other aspects of the rough boundaries, e.g., their excitations.

In summary, we have found that smooth open edges in the two-dimensional $S=\frac{1}{2}$ Heisenberg model have a smaller magnetic response than the bulk, contrary to the naively expected enhancement of fluctuations due to the smaller number of neighbors of the edge spins. We have explained this surprising effect in terms of local singlet formation at the edges, which in turn can be regarded as a consequence of entropy maximization in a valence-bond description of the system. In sharp contrast to smooth edges, rough boundaries lead to an enhanced magnetic susceptibility. We have argued that this is due to local sublattice imbalance ("dangling spins"), which impedes local singlet (short valance bond) formation. For both smooth and rough boundaries, the edge susceptibility of an infinite system diverges logarithmically as $T\rightarrow 0$. These studies also demonstrate that edges should have profound effects on the magnetic response of nanoscale clusters and that details of the boundary texture are important.

The smooth-edge effects that we have pointed out here were very recently examined using field-theoretical methods by Metlitski and Sachdev.[20] The negative edge susceptibility originates from low-lying spin waves. The prefactor of the logarithmic divergence, the slope in Fig. 1, is in reasonable agreement with the prediction of Ref. 20. The comb structure in the edge correlations was argued to be a short-distance phenomenon as we have also shown here, beyond the standard O(3) continuum field theory description. It can be understood in terms of proximity to a phase transition into a valence-bond solid state.

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